Effect of Cold Work and Partial Annealing on Thermomechanical Behaviour of Ti-50.5at%Ni

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ABSTRACT

This study investigated the effect of cold work and partial annealing on the thermal and mechanical behaviour of NiTi. It is well understood that the thermomechanical properties of near-equiatomic NiTi are highly dependent on the microstructure, hence the history of thermomechanical treatments it has undergone through. It has been generally accepted that a sufficiently high cold work is necessary prior to annealing but detailed knowledge of the influence of the level of prior cold work on annealing is unclear. This study determined the threshold effective levels of cold work required for annealing and demonstrated that the thermal and mechanical properties of Ti-50.5at%Ni are sensitive to the level of cold work as well as temperature of partial annealing.

Keywords: martensitic phase transformation, heat treatment, shape memory alloy, NiTi, superelasticity

1. INTRODUCTION

It is well known that properties of near-equiatomic Ni-Ti alloys are sensitive to their processing conditions, including cold work and annealing [1-4], precipitation ageing [5-7] and thermomechanical cycling [8, 9]. Cold working processes are applied to NiTi alloys in industrial production and laboratory treatment, such as sheet and wire rolling, tube extrusion and drawing, alloy hardening and shape setting. In this regard, knowledge of the effects of cold work and the subsequent heat treatment is of practical importance for both the production of the alloys and the design of shape memory apparatuses using these alloys.

It is known that desirable shape memory and pseudoelastic properties of near-equiatomic NiTi alloys are obtained with partial annealing at below the critical temperature for recrystallization. The effect of partial annealing provides a benchmark to understand and predict the deformation behaviours of the alloys at different application temperatures and also to design a desirable annealing temperature range for the required application temperature and stress. In this respect, much effort has been made in the past to characterise the effect of partial annealing of cold worked NiTi alloys on their thermal and mechanical properties. Most studies reported in the literature analysed the effect of annealing conditions on the martensitic transformation behaviour of the cold worked NiTi alloys [2, 10-15]. It has now been well established that cold work decreases the martensitic transformation temperatures and introduces the R-phase transformation [11, 16]. Partial annealing following cold work was also found effective in increasing the transformation temperatures [3, 17, 18]. Effect of short-time annealing on the superelastic behaviour of cold drawn NiTi wires has also been

reported, which showed that the best superelasticity can be obtained by annealing at 923 K for only 3 seconds [19]. Peterlechner et al. investigated the relaxation and crystallization behaviour of amorphous NiTi that underwent severe cold work, demonstrating that the crystallization kinetics agrees with Johnson-Mehl-Avrami model [20]. The microstructure evolution of the cold drawn amorphous NiTi wire during annealing has also been studied using Synchrotron high energy X-ray diffraction [21] and transmission electron microscopy [22-24].

Although the metallurgical principles of these effects are well established and the necessity of having sufficient pre-cold work is fully recognised to enable effective subsequent heat treatments, the knowledge of the critical level and the effect of different degrees of cold work on the alloy's response to annealing and the subsequent properties are scarce in the literature. The mapping of the effect of annealing has been achieved in the literature mostly from a "sufficiently high" level of cold work percentage (normally below 40%) prior to annealing [17, 25]. This has caused many to overlook the effect of cold work. Due to the lack of this knowledge, inconsistent results are obtained and reported in the literature of the properties of NiTi after partial annealing [11, 12, 16, 26].

This study investigates the influence of the level of cold work prior to partial annealing on the martensitic transformation and mechanical properties of Ti-50.5at%Ni. Such investigation provides a useful database for processing design for commercial production, property optimisation and apparatus design of shape memory.

2. EXPERIMENTAL PROCEDURE

The alloy used is a commercial superelastic Ti-50.5at%Ni wire of 1.4 mm in diameter. The wire was first solution treated at 1123 K for 3.6 ks in argon, followed by cold rolling at room temperature to different elongation percentages from 15% to 170% (corresponding to area reduction percentages from 13% to 63%) in multiple passes without intermediate annealing. The wires were rolled between the rollers with surface grooves which produced approximate hexagonal wire products. Following the cold working, the wire was annealed for 3.6 ks at different temperatures ranging from 573 K to 923 K in argon. Transformation behaviour of the annealed alloy was analysed by means of a TA instrument Q10 differential scanning calorimeter (DSC) at a heating and cooling rate of 10 K/min in N₂ atmosphere. The DSC measurements were conducted within a temperature range of 130-370 K and the sample mass was approximately 10 mg. Tensile deformation was conducted of the wire samples of 50 mm in gauge length using an Instron 4301 instrument with a test speed of 0.5 mm/min at 313 K.

3. RESULTS

3.1. Effect of Annealing Temperature

Figure 1 shows the evolution of thermal transformation behaviour of Ti-50.5at%Ni with respect to the variation of annealing temperature. The samples were previously cold rolled by 67% in elongation and subsequently annealed at different temperatures for 3.6 ks. The sample annealed at 873 K exhibited a single peak transformation of B2 $\leftrightarrow$ B19', representing a complete recrystallization of the microstructure [2, 13, 19]. The peak temperature for the forward transformation (B2 $\rightarrow$ B19') of this sample was measured to be $T^{A-M} = 280$ K and that for the reverse transformation (B19' $\rightarrow$ B2) was $T^{M-A} = 313$ K. When the deformed alloy was annealed at below the recrystallization temperature, the transformation preceded by

$B2 \rightarrow R \rightarrow B19'$ on cooling and $B19' \rightarrow B2$ on heating, as shown in the sample annealed at 823 K. Further lowering the annealing temperature to 723 K resulted in two-stage transformation behaviour of $B2 \leftrightarrow R \leftrightarrow B19'$ and reduced the transformation latent heat.

Figure 1. Thermal transformation behaviour of Ti-50.5at%Ni after partial annealing at different temperatures for one hour.

Figure 2 summarises the effect of annealing temperature on transformation behaviour, as extracted from Figure 1. Figure 2(a) shows the changes of transformation peak temperatures as a function of annealing temperature. The effect may be divided into two distinct regions in annealing temperature. Region I is above 845 K, where the alloy exhibited a single stage $B2 \leftrightarrow B19'$ martensitic transformation and the transformation temperatures appeared to be independent of the annealing temperature. This temperature (845 K) is identified the recrystallization completion temperature for this alloy, which is consistent with that reported by Miller et al [2]. Region II is below 845 K. In this region the alloy was partially annealed (partially recrystallized and recovered). The transformation sequence in this region was $B2 \rightarrow R \rightarrow B19'$ on cooling and $B19' \rightarrow B2$ on heating, which later evolved into $B19' \rightarrow R \rightarrow B2$ with lowering the annealing temperature. On cooling, $T^{R \rightarrow M}$ decreased rapidly and $T^{A \rightarrow R}$ increased steadily with decreasing annealing temperature, thus widening the apparent temperature interval of the transformations. Further decreasing the annealing temperature to below 660 K led to negligible change of transformation temperatures on both cooling and heating. However, the transformation peaks were further widened as the annealing temperature decreased.

Figure 2. Effect of annealing temperature on (a) transformation peak temperatures and (b) transformation latent heats of Ti-50.5at%Ni.

Figure 2(b) shows the effect of annealing temperature on the transformation enthalpy change. On heating, Δh^{M-A} represents the latent heat of B19'→B2 transformation and was measured from samples annealed at above 773 K. This latent heat decreased slowly as the annealing temperature decreased. Samples annealed at 723 K and below exhibited B19'→R→B2 transformations and the two transformation peaks overlapped, as seen in Figure 1. Therefore, the measured latent heat of Δh^{M-R-A} represents the combined heats of B19'→R (Δh^{M-R}) and R→B2 (Δh^{R-A}). Upon cooling, Δh^{A-M} represents the latent heat of single stage B2→B19' transformation measured from fully recrystallised samples. $\Delta h^{Total\ Cooling}$ represents the summation of latent heats measured separately from the A→R (Δh^{A-R}) and R→B19' (Δh^{R-M}) transformations. As the annealing temperature decreased, Δh^{A-R} remained nearly unaffected but Δh^{R-M} decreased severely. Comparing the total latent heats, it is seen that Δh^{M-R-A} (Δh^{M-A}) is always higher than $\Delta h^{Total\ Cooling}$.

Figure 3. Deformation behaviour of stress-induced martensitic transformation of Ti-50.5at%Ni samples annealed at different temperatures after 67% cold work.

Figure 3 shows the deformation behaviour of the alloy after partial annealing at different temperatures. The deformation was carried out in tension at 313 K. Samples annealed at 873 K and 923 K are fully recrystallised. They showed similar behaviour where the forward stress-induced martensite transformation occurred at about 170 MPa and the stress plateau

extended to about 10%, with 9% transformation strain. The critical stress to induce the forward transformation (σ^{fwd}) steadily increased as the annealing temperature decreased to below 823 K. Samples annealed at below 773 K showed good pseudoelasticity at the testing temperature of 313 K. The stress plateaus for the forward and the reverse transformations became less flat when annealing temperature decreased and the deformation behaviour gradually evolved into uniform deformation when annealing temperature was below 623 K. It is also apparent that the annealing temperature of 573 K was too low to induce adequate recovery in the matrix and therefore the deformation was in effect a mixed process of true plastic flow and martensitic transformation. The transformation plateau strain continued to decrease as the annealing temperature decreased.

Figure 4 summarises the results extracted from Figure 3, showing the effect of annealing temperature on the critical stresses and the transformation plateau strains for the forward and reverse stress-induced transformations. As seen in Figure 4(a), both the forward (σ^{fwd}) and the reverse (σ^{rev}) stresses increased as the annealing temperature decreased. σ^{rev} decreased more rapidly than σ^{fwd} , resulting in widening of the stress hysteresis (σ^{hys}) of pseudoelasticity with increasing annealing temperature. However, σ^{hys} remained nearly constant at about 250 MPa for the samples annealed at above 673 K. The reverse transformation was not expected to occur on unloading for samples annealed at above 823 K, since the deformation temperature was below or too close to the A_f temperature and also an addition of the effect of martensite stabilisation after the deformation, which shifted the A_f to higher temperatures.

Figure 4. Effect of annealing temperature on (a) the critical stresses and (b) plateau strains for the forward and the reverse stress-induced martensitic transformations.

Figure 4(b) shows the effect of annealing temperature on the forward (ϵ^{fwd}) and reverse (ϵ^{rev}) plateau strains. It is seen that both ϵ^{fwd} and ϵ^{rev} increased as the annealing temperature increased. It is also evident that $\epsilon^{\text{fwd}} > \epsilon^{\text{rev}}$. The maximum value of ϵ^{fwd} was ~9% after annealing at 873 K. Samples annealed at above 773 K showed no pseudoelasticity at this testing temperature. These results are consistent with previous studies [17, 27, 28]. The complete data shown in Figure 4 provides a useful guide for the design of NiTi materials via heat treatment for controlled properties, in particular functionally graded NiTi by means of heat treatment in gradient temperature fields.

3.2. Effect of Cold Work Percentage on Thermal Transformation Behaviour

Figure 5 shows the DSC measurements of samples which had been subjected to different elongation percentages (from 15% to 170%) of cold work. The samples were annealed at

three different temperatures below the recrystallization temperature to reveal the effect of prior deformation on partially annealed NiTi. Figure 5(a) shows the transformation behaviour of the wire samples annealed at 623 K, figure 5(b) shows the samples annealed at 723 K, and figure 5(c) shows the samples annealed at 823 K. Annealing at 623 K appears to have caused insufficient recovery and only weak transformations were observed, even for the lowest level of cold work of 15%. At 723 K, there is a clear progressive evolution of the transformation behaviour with respect to the level of the cold work. The temperature of the $R \rightarrow B19'$ transformation decreased with increasing level of the prior deformation. The $B2 \rightarrow R$ transformation remained at about the same temperature independent of the amount of cold work. Transformation on heating is also seen to split into two transformations of $B19' \rightarrow R$ and $R \rightarrow B2$ with increasing cold work. The $R \rightarrow B2$ transformation remained unchanged with respect to the level of the cold work. The samples annealed at 823 K, which is close to the recrystallization temperature (845 K), showed only very small variations relative to the samples annealed at 623K and 723 K in transformation behaviour for different levels of the prior cold work.

Figure 5. Effect of prior cold work on the thermal transformation behaviour of Ti-50.5at%Ni annealed at (a) 623 K, (b) 723 K and (c) 823 K.

Figure 6 shows the effect of cold work on the transformation temperatures of the samples annealed at different temperatures. Figure 6(a) shows the peak temperatures of the B19'→R (T^{M-R}) and R→B2 (T^{R-A}) reverse transformations on heating. Samples annealed at 823 K exhibited only single peak of B19'→B2 (T^{M-A}) upon heating and the temperature remained almost constant at 312 K for all levels of cold work, indicating that the samples annealed at 873 K have been fully recrystallised. Samples cold worked to 15% are not included in this figure, as their transformation involved only single peak of B19'→B2. This implies that internal resistance created in the matrix from 15% of cold work was thermodynamically insufficient to induce R-phase on the reverse transformation. T^{M-R} dropped by ~10 K when the level of cold work was increased from 35% to 95% for all annealing temperatures. Excessive cold working beyond 95% caused no change to this transformation temperature. On the other hand, T^{R-A} remained almost constant for all levels of cold work. However, lowering the annealing temperature from 723 K to 623 K caused T^{R-A} to increase by more than 10 K at all levels of cold work.

Figure 6. Effect of cold work on transformation temperatures: (a) heating transformations and (b) cooling transformations.

Figure 6(b) shows the peak temperatures of the B2→R (T^{A-R}) and R→B19' (T^{R-M}) forward transformations upon cooling. The T^{A-M} value of the fully recrystallized samples annealed at 873 K are also included for direct comparison with the partially annealed samples. It is seen that T^{A-R} for each annealing temperature remained constant regardless of the level of cold work. However, lowering the annealing temperature from 823 K to 623 K caused T^{A-R} to increase by as much as 40 K. Meanwhile, T^{R-M} drastically decreased as the level of cold work increased for all samples annealed at below 723 K, with the maximum effect being achieved from the sample annealed at 623 K. The effect was much reduced for annealing temperatures above 773 K.

Figure 7 shows the tensile deformation behaviour of the cold worked samples after annealing at different temperatures. The testing temperature was 313 K for all samples. Figure 7(a) shows all samples annealed at 773 K. The samples showed similar critical stresses for the forward stress-induced transformation at $\sigma^{\text{fwd}} \sim 280$ MPa except for the sample deformed by 15% cold work which shows the stress-induced transformation occurring at ~ 200 MPa. The stresses for the reverse transformation also remained at similar levels for all samples cold worked for more than 35%, but no pseudoelasticity was achieved for the sample cold worked by 15%. Figure 7(b) shows the deformation behaviour of the samples annealed at 723 K. The samples showed a progressive increase in stress for inducing the forward transformation with increasing the level of cold work from 15% to 67%. Above 67% cold work, the samples showed a similar stress for inducing the martensitic transformation, at ~ 350 MPa. Again, no pseudoelasticity was observed for the sample cold worked by 15%. Figure 7(c) shows the deformation behaviour of the samples annealed at 673 K. These samples show an obvious progressive increase of σ^{fwd} with respect to the level of cold work. The sample cold worked by 15% showed a partial pseudoelasticity. Figure 7(d) shows the deformation behaviour of the samples annealed at 623 K. The samples showed a more progressive increasing tendency of σ^{fwd} with respect to the level of cold work. The σ^{fwd} of sample cold worked at 170% shows a value of ~ 550 MPa. The 15% cold-worked sample showed a good pseudoelastic strain recovery with only 1.5% permanent strain following unloading. At the meantime, the Lüders type characteristics of the samples seem to have been weakened.

Figure 7. Tensile deformation behaviour of Ti-50.5at%Ni at 313 K after annealing at (a) 773 K, (b) 723 K, (c) 673 K and (d) 623 K.

Figure 8 summarises the effect of the level of cold work on the critical stresses for the forward and reverse stress-induced martensitic transformations. As seen in Figure 8(a), the stresses for the forward transformation remained nearly the same at ~170 MPa for the fully annealed samples (above 873 K) regardless of the amount of cold work. Similarly, annealing at 823 K and 773 K revealed almost negligible influence of the cold work on the transformation stress. The increase of stress level as compared to the fully annealed samples is mainly due to the annealing temperature effect. The effect of cold work percentage is more obvious when the annealing temperature is below 723 K. As seen in the figure, the critical stress of the sample cold worked by 67% is ~130 MPa higher than that of the sample cold worked by 15% for annealing at 723 K. However, the increase of this critical stress stabilised at 67% of cold work. Further increase of cold work percentage did not cause the critical stress to increase further. This implies that increasing the level of cold work to beyond 67% produces no advantage on improving the yield strength of the alloy after annealing at this temperature. Nevertheless, further lowering of annealing temperature to 623 K allows the alloy to deform via stress-induced transformation at a maximum value of 550 MPa when the percentage of cold work reached 170%. This stress is ~330 MPa above that of the sample cold worked by 15%. Similar phenomenon was also observed for the critical stress for the reverse transformation, as seen in Figure 8(b). Annealing at a high temperature of 773 K erased all influence of cold work on the critical stress for the reverse transformation. Annealing at and below 673 K was found to be effective in preserving the increase of yield strength with respect to the increase of cold work percentage.

Figure 8. Effect of cold work on the critical stress for stress-induced martensitic transformation (SIMT): (a) forward transformation and (b) reverse transformation.

Figure 9 shows the effect of annealing temperature on the critical stresses for stress-induced martensitic transformation with respect to the level of cold work. The figure is based on the experimental data shown in Figure 7. Figure 9(a) shows the effect on the forward transformation and Figure 9(b) shows the effect on the reverse transformation. As seen in (a), the stress for the forward transformation decreased continuously with increasing annealing temperature and stabilised at above 845 K. This stabilisation was reached at the same temperature for all samples regardless of the level of cold work. This implies that increasing the cold work percentage did not affect the recrystallization temperature. As seen in (b), cold working by 15% produced only minimal improvement to the yield strength and consequently poor pseudoelasticity. Cold work between 35% and 95% seems to be the optimum range for enhancing shape memory behaviour of this alloy. Excessive cold working to beyond 170% is seen to be unnecessary.

Figure 9. Effect of annealing temperature on the critical stress for inducing martensitic transformation: (a) forward transformation and (b) reverse transformation.

4. DISCUSSION

It is seen in Figures 8 and 9 that the critical stresses to induce the martensitic transformation in the partially annealed samples increase with increasing the level of prior cold work. For the fully recrystallized samples, the effect of prior cold work is totally eliminated. The actual stress for inducing the martensitic transformation is determined by two contributing factors, as:

$$\sigma^{fwd}(T) = \sigma_{mech}^{fwd} + \sigma_{therm}^{fwd}(T) \quad (1)$$

where σ_{mech}^{fwd} is the mechanical resistance to the deformation associated with the stress-induced martensitic transformation of the matrix and $\sigma_{therm}^{fwd}(T)$ is the thermodynamic resistance to the phase transformation caused by the temperature deficit ($T - T^{A-M}$). It is worth noting that the transformation temperatures presented in Figure 6 are for R→M (T^{R-M}), whereas the stress induced transformation is A→M (σ^{A-M}). To take this into account, T^{A-M} can be estimated based on the free energy relation as [29]:

$$T^{A-M} = \frac{\Delta H^{A-R} + \Delta H^{R-M}}{\left(\frac{\Delta H^{A-R}}{T^{A-R}}\right) + \left(\frac{\Delta H^{R-M}}{T^{R-M}}\right)} \quad (2)$$

Using the measured values of $\Delta h^{A-R} = 5.5$ J/g and $\Delta h^{R-M} = 12.5$ J/g (from the sample annealed at 823 K) for this alloy system, T^{A-M} for the 67% cold-worked samples are calculated and the results are shown in Figure 10 with respect to annealing temperature. The calculated T_s^{A-M} represents the estimated starting temperature of B2→B19' transformation (which is thermodynamically prohibited in the samples), T_s^{A-R} is the measured starting temperature of A→R transformation and T_s^{R-M} is the measured starting temperature of R→M transformation. The measured peak temperatures of B2→B19' (*peak* T^{A-M}) and R→B19' (*peak* T^{R-M}) are also included in the figure for comparison. Similarly, the measured starting temperatures of B2→B19' (T_s^{A-M}) from the fully recrystallised samples are also included, and are artificially

connected with the calculated T_s^{A-M} curve. This illustrates the validity and continuity of the calculation with the experiment.

Figure 10. Effect of annealing temperature on T_s^{A-M} as determined from equation (2). The data are for 67% cold-worked samples.

Using the interpolated value of T_s^{A-M} , $\sigma_{therm}^{fwd}(T)$ can be estimated using the Clausius-Clapeyron relation. Taking $\frac{d\sigma}{dT} = 5 \text{ MPa} / \text{K}$ [30], $\sigma_{therm}^{fwd}(T)$ are calculated as:

$$\sigma_{therm}^{fwd}(T) = (T - T_s^{A-M}) \frac{d\sigma}{dT} \quad (3)$$

The results of $\sigma_{therm}^{fwd}(T)$ for the samples annealed at different temperatures are plotted in Figure 11. The measured values of $\sigma_{therm}^{fwd}(313K)$ are also included in the figure for comparison. Following Equation 1, the difference between $\sigma_{therm}^{fwd}(313K)$ and σ_{therm}^{fwd} is obviously the mechanical resistance of the matrix to deformation of the stress-induced martensitic transformation, denoted σ_{mech}^{fwd} . It is evident that σ_{therm}^{fwd} decreased with increasing annealing temperature, which is obviously caused by the increase of T_s^{A-M} with increasing annealing temperature, whereas σ_{mech}^{fwd} remained practically constant at ~40 MPa except for the sample annealed at 673 K which is 83 MPa.

Figure 11. Effect of annealing temperature on thermodynamic stress σ_{therm}^{fwd} and mechanical stress σ_{mech}^{fwd} required for inducing B2-B19' martensitic transformation in Ti-50.5at%Ni.

Figure 12 shows the comparison of the measured σ^{fwd} and the calculated σ_{therm}^{fwd} as functions of the percentage of cold work for annealing at 723 K, 823 K and 873 K. It is evident that σ_{therm}^{fwd} followed the trend of σ^{fwd} for all the three conditions, implying that variation of the transformation stress is mostly caused by variation of the transformation temperature. It is also evident that σ_{mech}^{fwd} changed much less significantly with respect to the percentage of cold work for all the three annealing temperatures. The increase of critical stress for transformation by the increase of cold work percentage is mainly due to the suppression of transformation temperature, particularly B2→B19'. Meanwhile, the mechanical resistance σ_{mech}^{fwd} was considered less sensitive to the annealing temperature or cold work percentage.

Figure 12. Effect of cold work percentage on thermodynamic stress σ_{therm}^{fwd} and mechanical stress σ_{mech}^{fwd} for inducing B2→B19' martensitic transformation in Ti-50.5at%Ni.

5. CONCLUSIONS

This study investigated the effect of cold work and partial annealing on the transformation and deformation behaviour of Ti-50.5at%Ni alloy. The study provides a complete data set for evaluating the severity of cold work and its impact on partial annealing and the subsequent property changes of NiTi. Such data is of practical use for NiTi materials production and quality control. The main findings of this study may be summarized as following:

- (1) Severe cold work suppresses the B2→B19' martensitic transformation and introduces the B2→R transformation. The recrystallization temperature of the Ti-50.5at%Ni alloy is determined to be ~ 845 K. The level of prior cold work has no effect on the properties of the alloy after full recrystallization annealing. For partially annealed samples, the level of prior cold work had clear influence on the outcomes of the annealing. The minimum cold work required is 15% wire rolling elongation.
- (2) Good pseudoelasticity may be achieved in Ti-50.5at%Ni alloy at 313 K by cold work and partial annealing at between 623 K and 773 K. The critical plateau stresses of pseudoelasticity increases with increasing the level of prior cold work for partially annealed samples. For a given prior cold work, the critical plateau stresses of pseudoelasticity increases with decreasing annealing temperature.
- (3) The increase of transformation stress is mainly caused by the increase of thermodynamic resistance due to the suppression of the transformation temperatures, particularly that of B2→B19'. The mechanical resistance to stress-induced transformation is a minor contributor to transformation stress and is less sensitive to the percentage of cold work for all annealing temperatures.

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